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(54) Title: THERMOSET ELASTOMERS.

(57) Abstract

The subject invention provides a thermoset elastomer comprising a crosslinked pseudorandom or substantially random interpolymer of: (a) from 15 to 70 weight percent of at least one α -olefin, (b) from 30 to 70 weight percent of at least one vinylidene aromatic compound, and (c) from 0 to 15 weight percent of at least one diene. The subject invention further provides provides a thermoplastic vulcanizate comprising the thermoset elastomers of the invention as provided in a thermoplastic polyolefin matrix. The subject invention further provides processes for preparing the inventive thermoset elastomers and thermoplastic vulcanizates, as well as parts fabricated therefrom. The inventive materials have a superior balance of properties, as compared to EPM and EPDM based materials.

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THERMOSET ELASTOMERS

The subject invention pertains to thermoset elastomers, to a process for their preparation, and to products fabricated from such elastomers.

Elastomers are defined as materials which experience large reversible deformations under relatively low stress. Elastomers are typically characterized as having structural irregularities, non-polar structures, or flexible units in the polymer chain. Some examples of commercially available elastomers include natural rubber, ethylene/propylene (EPM) copolymers, ethylene/propylene/diene (EPDM) copolymers, styrene/butadiene copolymers, chlorinated polyethylene, and silicone rubber.

Thermoplastic elastomers are elastomers having thermoplastic properties. That is, thermoplastic elastomers may be molded or otherwise shaped and reprocessed at temperatures above their melting or softening point. One example of thermoplastic elastomers is styrene-butadiene-styrene (SBS) block copolymers. SBS block copolymers exhibit a two phase morphology consisting of glassy polystyrene domains connected by rubbery butadiene segments. At temperatures between the glass transition temperatures of the butadiene midblock and the styrene endblocks, that is, at temperatures from -90°C to 116°C, the SBS copolymers act like a crosslinked elastomer.

European Patent Publication 416,815 discloses pseudorandom ethylene-styrene interpolymers. Uncrosslinked pseudorandom ethylene/styrene interpolymers exhibit a decreased modulus at temperatures above the melting or softening point of the interpolymers.

SBS copolymers and uncrosslinked ethylene-styrene pseudorandom interpolymers suffer the disadvantages of relatively low mechanical strength, susceptibility to ozone degradation (to the extent that they have sites of unsaturation in the polymer backbone), and utility in only applications where the temperature of the elastomer will not exceed the melting or softening point of the elastomer.

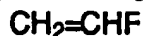
In contrast, thermoset elastomers are elastomers having thermoset properties. That is, thermoset elastomers irreversibly solidify or "set" when heated, generally due to an irreversible crosslinking reaction. Two examples of thermoset elastomers are crosslinked ethylene-propylene monomer rubber (EPM) and crosslinked ethylene-propylene-diene monomer rubber (EPDM). EPM materials are made by the copolymerization of ethylene and propylene. EPM materials are typically cured with peroxides to give rise to crosslinking, and thereby induce thermoset properties. EPDM materials are linear interpolymers of ethylene, propylene, and a nonconjugated diene such as 1,4-hexadiene, dicyclopentadiene, or ethylidene norbornene. EPDM materials are typically vulcanized with sulfur to induce thermoset properties, although they alternatively may be cured with peroxides. While EPM and EPDM materials are advantageous in that they have applicability in higher temperature applications, EPM and EPDM elastomers suffer the disadvantages of low green strength (at lower ethylene contents), of a higher susceptibility of the cured elastomer to attack by oils than characteristic of styrene butadiene rubbers, and of resistance of the cured elastomer to surface modification.

fracture is characterized at the beginning of losing extrudate gloss at which the surface roughness of extrudate can only be detected by 40 X magnification. Gross melt fracture occurs at unsteady flow conditions and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. The critical shear rate at the onset of surface melt fracture and onset of gross melt fracture, as used herein, are based on the changes of surface roughness and configurations of the extrudates extruded by a GER.

Substantially linear interpolymers of ethylene and styrene are disclosed in USP 5,272,236 and USP 5,272,236, and in U.S. Patent Application Serial Nos. 08/166,789 to inventors Lai et al. filed on December 13, 1993 and 08/166,412 to inventors Lai et al. filed on December 13, 1993, the disclosures of which are incorporated herein by reference.

The α -olefin Monomer

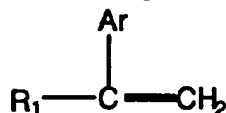
Suitable α -olefins are represented by the following formula:



where R is hydrogen or a hydrocarbyl radical having from one to twenty carbon atoms. Typical α -olefins include, for example, ethylene, propylene, 1-butene, 3-methyl-1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 5-methyl-1-hexene, 4-ethyl-1-hexene, 1-octene, 1-dodecene, 3-phenylpropene, and mixtures thereof. Preferably, the α -olefin will comprise ethylene, or a mixture of ethylene with another α -olefin, such as 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, or 1-octene.

The Vinylidene Aromatic Monomer

Suitable vinylidene aromatic monomers are represented by the following formula:



wherein R_1 is selected from the group of radicals consisting of hydrogen and alkyl radicals containing three carbons or less, and Ar is selected from the group of radicals consisting of phenyl, halophenyl, alkylphenyl, and alkylhalophenyl. Exemplary vinylidene aromatic monomers include styrene; α -methylstyrene; the C1-C4 alkyl- or phenyl- ring substituted derivatives of styrene, such as ortho-, meta-, and para-methylstyrene, or mixtures thereof; the ring halogenated styrenes such as chlorostyrene; vinylbenzocyclobutanes; and divinylbenzene. Styrene is a particularly desirable vinylidene aromatic monomer used in the practice of the present invention.

The level of vinylidene aromatic monomer incorporated in the thermoset elastomers of the invention is at least 30, preferably at least 35 weight percent based on the weight of the interpolymers. The vinylidene aromatic monomer is typically incorporated in the interpolymers of the invention in an amount less than 70, more typically less than 60 weight percent based on the weight of the interpolymers.

The Diene:

One or more dienes can optionally be incorporated into the interpolymer to provide functional sites of unsaturation on the interpolymer useful, for example, to participate in crosslinking reactions. While conjugated dienes such as butadiene, 1,3-pentadiene (that is, piperylene), or isoprene may be used for this purpose, nonconjugated dienes are preferred. Typical nonconjugated dienes include, for example
5 the open-chain nonconjugated diolefins such as 1,4-hexadiene (see U.S. Patent No. 2,933,480) and 7-methyl-1,6-octadiene (also known as MOCD); cyclic dienes; bridged ring cyclic dienes, such as dicyclopentadiene (see U.S. Patent No. 3,211,709); or alkylidenenorbornenes, such as methylenenorbornene or ethylenenorbornene (see U.S. Patent No. 3,151,173). The nonconjugated dienes are not limited to those having only two double bonds, but rather also include those having three
10 or more double bonds.

The diene is incorporated in the elastomers of the invention in an amount of from 0 to 15 weight percent based on the total weight of the interpolymer. When a diene is employed, it will preferably be provided in an amount of at least 2 weight percent, more preferably at least 3 weight percent, and most preferably at least 5 weight percent, based on the total weight of the interpolymer.
15 Likewise, when a diene is employed, it will be provided in an amount of no more than 15, preferably no more than 12 weight percent based on the total weight of the interpolymer.

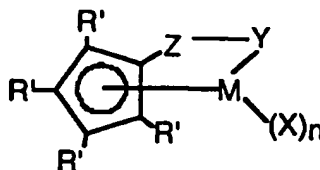
Preparation of the substantially random/pseudorandom interpolymers:

The substantially random/pseudorandom interpolymers may be prepared via the solution, slurry, or gas phase interpolymerization of the α -olefin, the vinylidene aromatic compound, and the
20 optional diene, in the presence of an olefin polymerization catalyst comprising a metal coordination complex and activating cocatalyst, such as are described in European Patent Publications 416,815-A, 468,651-A, 514,828-A, and 520,732-A, in U.S. Patent Application Serial No. 8,003, filed January 21, 1993, and in U.S. Patent Nos. 5,055,438, 5,057,475, 5,096,867, 5,064,802 and 5,132,380, the disclosures of which are incorporated herein by reference. Also suitable in the practice of the claimed invention are
25 the monocyclopentadienyl transition metal olefin polymerization catalysts taught in USP 5,026,798, as well as the catalysts disclosed in European Patent Publication 572,990-A2, the disclosures of which are incorporated herein by reference.

The foregoing catalysts may be further described as comprising a metal coordination complex comprising a metal of Group III or IV or the Lanthanide series of the Periodic Table of the Elements and
30 a delocalized Π -bonded moiety substituted with a constrain-inducing moiety, said complex having a constrained geometry the metal atom such that the angle at the metal between the centroid of the delocalized, substituted Π -bonded moiety and the center of at least one remaining substituent is less than such angle in a similar complex containing a similar Π -bonded moiety lacking in such constrain-inducing substituent, and provided further that for such complexes comprising more than one
35 delocalized, substituted π -bonded moiety, only one thereof for each metal atom of the complex is a

cyclic, delocalized, substituted π -bonded moiety. The catalyst further preferably comprises an activating cocatalyst.

1. The metal coordination complex. The metal coordination complex employed will preferably correspond to the following formula:



5 wherein R' at each occurrence is independently selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, each said R' having up to 20 non-hydrogen atoms, and with two R' groups (where R' is not hydrogen, halo, or cyano) being optionally joined together to form a divalent derivative thereof connected to adjacent positions of the
10 cyclopentadienyl ring to form a fused ring structure;

X at each occurrence independently is selected from the group consisting of hydride, halo, hydrocarbyl, silyl, germyl, hydrocarbyloxy, amido, siloxy, and combinations thereof, each said X having up to 20 non-hydrogen atoms; or when M is in the +3 oxidation state, X is preferably a stabilizing ligand comprising an amine, phosphine, ether or thioether functionality able to form a coordinate-covalent bond
15 or chelating bond with M , or (when X is a hydrocarbyl) an ethylenic unsaturation able to form an η^3 bond with M ;

Y is a divalent anionic ligand group comprising nitrogen, phosphorus, oxygen or sulfur (preferably $-O^-$, $-S^-$, $-NR^*-$, or $-PR^*-$) and having up to 20 non-hydrogen atoms, said Y being bonded to Z and M through said nitrogen, phosphorus, oxygen or sulfur, with Y and Z being optionally joined
20 together to form a fused ring system;

M is a Group 4 metal, especially titanium;

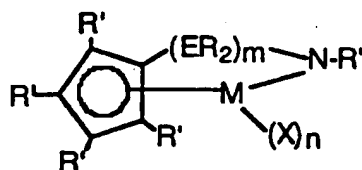
Z is SiR^*2 , CR^*2 , SiR^*2SiR^*2 , CR^*2CR^*2 , $CR^*=CR^*$, CR^*2SiR^*2 , GeR^*2 , BR^* , or BR^*2 ;

wherein:

R^* at each occurrence is independently selected from the group consisting of hydrogen,
25 hydrocarbyl, silyl, halogenated hydrocarbyl groups having up to 20 non-hydrogen atoms, and combinations thereof, with two R^* groups from Z (when R^* is not hydrogen) or an R^* group from Z (when R^* is not hydrogen) and an R^* group from Y (when R^* is not hydrogen) being optionally joined to form a fused ring system; and

n is 1 or 2.

30 The most preferred metal coordination complexes are amidosilane- or amidoalkanedyl- compounds corresponding to the following formula II:



wherein:

M is titanium bound in an η^5 bonding mode to the cyclopentadienyl group;

R' at each occurrence is independently selected from the group consisting of hydrogen, silyl, hydrocarbyl, and combinations thereof, each said R' having up to 10 carbon or silicon atoms, or with two R' groups (when R' is not hydrogen) being joined together to form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

E is silicon or carbon;

X is independently at each occurrence hydride, halo, hydrocarbyl, or hydrocarbyloxy, each said X having up to 10 carbons, or when M is in the +3 formal oxidation state, X is preferably a stabilizing ligand such as a hydrocarbyl, silyl, amido or phosphido ligand substituted with one or more aliphatic or aromatic ether-, thioether-, amine- or phosphine- functional groups, especially such amine or phosphine groups that are tertiary substituted, said stabilizing ligand having from 3 to 30 nonhydrogen atoms, or X is a C₃₋₁₅ hydrocarbyl group containing ethylenic unsaturation;

m is 1 or 2; and

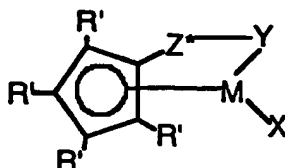
n is 1 or 2.

Examples of these most preferred metal coordination complexes include compounds wherein the R' on the amido group is methyl, ethyl, propyl, butyl, pentyl, or hexyl (including isomers of these alkyls) norbornyl, benzyl, phenyl, etc.; the cyclopentadienyl group is cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, octahydrofluorenyl, tetrahydrofluorenyl, etc.; R' on the foregoing cyclopentadienyl groups is independently at each occurrence hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, norbornyl, benzyl, phenyl, etc.; and X is chloro, bromo, iodo, methyl, ethyl, propyl, butyl, pentyl, hexyl (including isomers of these alkyls), norbornyl, benzyl, phenyl, etc, or when M is in the +3 formal oxidation state, X is most preferably 2-dialkylaminobenzyl or 2-(dialkyl-aminomethyl)phenyl groups containing from 1 to 4 carbons in the alkyl groups, or an allyl, 1-methylallyl, 2-methylallyl, 1,1-dimethylallyl, 1,2,3-trimethylallyl, 1-phenyl-3-benzylallyl or 1,1-diphenyl-3-(diphenylmethyl)allyl group.

Specific embodiments of these most preferred metal coordination complexes include (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediytzirconium dichloride; (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyttitanium dichloride; (methylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediytzirconium dichloride; (methylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyttitanium dichloride; (ethylamido)(tetramethyl- η^5 -cyclopentadienyl)methylenetitanium dichloride; (tert-butylamido)dimethyl(tetramethyl- η^5 -

cyclopentadienyl)silane titanium dimethyl; (tert-butylamido)dimethyl (tetramethyl- η 5-cyclopentadienyl)silane zirconium dibenzyl; (benzylamido)dimethyl (tetramethyl- η 5-cyclopentadienyl)silane titanium dichloride; and (phenylphosphido)-dimethyl (tetramethyl- η 5-cyclopentadienyl)silane zirconium dibenzyl.

- 5 Other preferred monocyclopentadienyl metal coordination complexes useful to prepare the interpolymers will include titanium or zirconium in the +2 formal oxidation state and will correspond to the following formula III:



wherein:

- 10 R' at each occurrence is independently selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, each said R' having up to 20 non-hydrogen atoms, with two R' groups (when R' is not hydrogen, halo or cyano) being optionally joined together to form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;
- 15 X is a neutral η 4-bonded diene group having up to 30 non-hydrogen atoms, which forms a Π -complex or a σ -complex with M (as disclosed in U.S. Patent Serial No. 241,523, filed on May 12, 1994 or U.S. Patent Serial No. 267,993, filed on June 28, 1994, the disclosures of which are incorporated herein by reference);
- Y is -O-, -S-, -NR^{*}-, -PR^{*}-;
- 20 M is titanium or zirconium in the +2 formal oxidation state;
- Z^{*} is SiR^{*}₂, CR^{*}₂, SiR^{*}₂SiR^{*}₂, CR^{*}₂CR^{*}₂, CR^{*}=CR^{*}, CR^{*}₂SiR^{*}₂, or GeR^{*}₂, wherein:
- R^{*} at each occurrence is independently hydrogen, or a member selected from the group consisting of hydrocarbyl, silyl, halogenated hydrocarbyl, and mixtures thereof, each said R^{*} having up to 20 non-hydrogen atoms, with two R^{*} groups from Z^{*} (where R^{*} is not hydrogen), or an R^{*} group from Z^{*} (where R^{*} is not hydrogen) and an R^{*} group from Y (where R^{*} is not hydrogen) being optionally joined to form a fused ring system. These are disclosed in full in U.S. Application Serial No. 82,197, filed June 24, 1993, the relevant portions of which are incorporated herein by reference.

2. The activating cocatalyst. The activating cocatalyst is employed to cause the metal coordination complex to become effective as an addition polymerization catalyst or to balance the ionic charge of a catalytically activated metal coordination complex. Suitable cocatalysts for use herein include polymeric or oligomeric alumoxanes, especially methylalumoxane and modified methyl alumoxane; polymeric, oligomeric or monomeric carbylboranes, especially tris(pentafluorophenyl)borane; aluminum alkyls; aluminum halides; haloaluminum alkyls; other strong

Lewis acids; ammonium salts; oxidizing agents, such as silver salts, ferrocenium ions, etc; and mixtures of such cocatalysts. Preferred cocatalysts are noninterfering, noncoordinating, ion-forming boron compounds, such as tris(pentafluorophenyl)borane.

Alumoxanes can be made as disclosed in U.S. Patent Nos. 5,542,199; 4,544,762; 5,015,749; 5 and 5,041,585, the disclosures of which are incorporated herein by reference. So called modified methyl alumoxane (MMAO) is also suitable for use as a cocatalyst. One technique for preparing such modified alumoxane is disclosed in U.S. Patent No. 5,041,584, the disclosure of which is incorporated herein by reference.

3. Preparation of the active metal coordination complexes. Active catalyst species, that is, the 10 catalysts resulting from the combination of the metal coordination complexes and an activating cocatalyst, can be prepared via any of the following techniques:

A. As disclosed in U.S. patent 5,064,802 and 5,132,38, the disclosure of which is incorporated herein by reference, the metal coordination complex containing at least one substituent (preferably at least one hydrocarbyl or substituted hydrocarbyl group) is combined with the cation of a second 15 component which is a Bronsted acid and a noncoordinating compatible anion (such as substituted ammonium salts, for example, N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate);

B. As disclosed in PCT Application 93/23412, the disclosure of which is incorporated herein by reference, the metal coordination complex is combined with at least one second component which is a salt of a carbenium and a noncoordinating, compatible anion;

20 C. As disclosed in U.S. Patent No. 5,189,192, the relevant portions of which are incorporated herein by reference, a reduced metal derivative of the desired metal coordination complex wherein the metal is in an oxidation state one less than that of the metal in the finished complex is combined with at least one second component which is a salt of a cationic oxidizing agent and a noncoordinating, compatible anion;

25 D. As disclosed in U.S. Patent Application Serial No. 08/34,434, filed March 19, 1993, the relevant portions of which are incorporated herein by reference, a reduced metal derivative of the desired metal coordination complex wherein the metal is in an oxidation state one less than that of the metal in the finished complex is combined with at least one second component which is a neutral oxidizing agent (such as quinone compounds, especially bisquinones) in combination with a Lewis acid mitigating agent 30 (such as tris(perfluorophenyl)borane); or

E. As disclosed in European Patent Publication 520,732-A, the relevant portions of which are incorporated herein by reference, the metal coordination complex (preferably containing at least one hydride, hydrocarbyl or substituted hydrocarbyl group able to be abstracted by a Lewis acid) is combined with a Lewis acid having sufficient Lewis acidity to cause abstraction of an anionic ligand of 35 the metal coordination complex thereby forming a cationic derivative thereof (such as tris(perfluorophenyl)-borane).

4. The Polymerization Reaction. The conditions for polymerizing the α -olefin, vinylidene aromatic, and optional diene are generally those useful in the solution polymerization process, although the application of the present invention is not limited thereto. High pressure, slurry and gas phase polymerization processes are also believed to be useful, provided the proper catalysts and polymerization conditions are employed.

In general, the polymerization useful in the practice of the subject invention may be accomplished at conditions well known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerizations. In particular, the polymerization will typically involve pressures from atmospheric up to 1000 atmospheres (100 MPa) and temperatures from 0°C to 250°C.

While polymerizing and isolating the substantially random/pseudorandom interpolmer, a small amount of atactic vinylidene aromatic homopolymer may be formed due to homopolymerization of the vinylidene aromatic monomer. In general, the higher the polymerization temperature is, the higher is the amount of homopolymer formed. If desired, the vinylidene aromatic homopolymer may be at least partially separated from the substantially random/pseudorandom interpolmer, if desired, such as by extraction with a suitable extracting solvent.

The substantially random/pseudorandom interpolymers may be modified by typical grafting, crosslinking, hydrogenation, functionalizing, or other reactions well known to those skilled in the art, provided that the elastomeric properties of the interpolymers are not substantially affected. The polymers may be readily sulfonated or chlorinated to provide functionalized derivatives according to established techniques.

Compounding and Curing the Substantially Random/Pseudorandom Interpolymers

The thermoset elastomers of the invention may include various additives, such as carbon black, silica, titanium dioxide, colored pigments, clay, zinc oxide, stearic acid, accelerators, curing agents, sulfur, stabilizers, antidegradants, processing aids, adhesives, tackifiers, plasticizers, wax, precrosslinking inhibitors, discontinuous fibers (such as wood cellulose fibers) and extender oils. Such additives may be provided either prior to, during, or subsequent to curing the substantially random/pseudorandom interpolymers. The substantially random/pseudorandom interpolymers are typically mixed with a filler, an oil, and a curing agent at an elevated temperature to compound them. The compounded material is the subsequently cured at a temperature which is typically greater than that employed during compounding.

Preferably, carbon black will be added to the substantially random/pseudorandom interpolmer prior to curing. Carbon black is typically added to improve the tensile strength or toughness of the compounded product, but can also be used as an extender or to mask the color of the compounded product. Carbon black will typically be provided in an amount from 0 to 80 weight percent, typically from 0.5 to 50 weight percent, based on the total weight of the formulation. When the carbon black is employed to mask a color, it is typically employed in the range of 0.5 to 10 weight percent, based on

the weight of the formulation. When the carbon black is employed to increase toughness and/or decrease the cost of the formulation, it is typically employed in amounts greater than 10 weight percent based on the weight of the formulation.

Moreover, preferably, one or more extender oils will be added to the substantially
5 random/pseudorandom interpolmer prior to curing. Extender oils are typically added to improve processability and low temperature flexibility, as well as to decrease cost. Suitable extender oils are listed in Rubber World Blue Book 1975 Edition, Materials and Compounding Ingredients for Rubber, pages 145-190. Typical classes of extender oils include aromatic, naphthenic, and paraffinic extender oils. The extender oil(s) will typically be provided in an amount from 0 to 50 weight percent. When
10 employed, the extender oil will typically be provided in an amount of at least 5 weight percent, more typically in an amount of from 15 to 25 weight percent, based on the total weight of the formulation.

The curing agent(s) will typically be provided in an amount of from 0.5 to 12 weight percent, based on the total weight of the formulation.

Suitable curing agents include peroxides, phenols, azides, aldehyde-amine reaction products,
15 substituted ureas, substituted guanidines; substituted xanthates; substituted dithiocarbamates; thiazoles, imidazoles, sulfenamides, thiuramidisulfides, paraquinonedioxime, dibenzoparaquinonedioxime, sulfur, and combinations thereof. See Encyclopedia of Chemical Technology, Vol. 17, 2nd edition, Interscience Publishers, 1968; also Organic Peroxides, Daniel Seem, Vol. 1, Wiley-Interscience, 1970).

Suitable peroxides include aromatic diacyl peroxides; aliphatic diacyl peroxides; dibasic acid
20 peroxides; ketone peroxides; alkyl peroxyesters; alkyl hydroperoxides (for example, diacetylperoxide; dibenzoylperoxide; bis-2,4-dichlorobenzoyl peroxide; di-tert-butyl peroxide; dicumylperoxide; tert-butylperbenzoate; tert-butylcumylperoxide; 2,5-bis (t-butylperoxy)-2,5-dimethylhexane; 2,5-bis (t-butylperoxy)-2,5-dimethylhexyne-3; 4,4',4'-tetra-(t-butylperoxy)-2,2-dicyclohexylpropane; 1,4-bis-(t-butylperoxyisopropyl)-benzene; 1,1-bis-(t-butylperoxy)-3,3,5-trimethylcyclohexane; lauroyl peroxide;
25 succinic acid peroxide; cyclohexanone peroxide; t-butyl peracetate; butyl hydroperoxide; etc.

Suitable phenols are disclosed in USP 4,311,628, the disclosure of which is incorporated herein by reference. One example of a phenolic cure agent is the condensation product of a halogen substituted phenol or a C₁-C₁₀ alkyl substituted phenol with an aldehyde in an alkaline medium, or by condensation of bifunctional phenoldialcohols. One such class of phenolic cure agents is dimethylol phenols
30 substituted in the para position with C₅-C₁₀ alkyl group(s). Also suitable are halogenated alkyl substituted phenol curing agents, and cure systems comprising methylol phenolic resin, a halogen donor, and a metal compound.

Suitable azides include azidoformates, such as tetramethylenebis(azidoformate) (see, also, USP 3,284,421, Breslow, Nov. 8, 1966); aromatic polyazides, such as 4,4'-diphenylmethane diazide (see,
35 also, USP 3,297,674, Breslow et al., Jan. 10, 1967); and sulfonazides, such as p,p'-oxybis(benzene sulfonyl azide).

Suitable aldehyde-amine reaction products include formaldehyde-ammonia; formaldehyde-ethylchloride-ammonia; acetaldehyde-ammonia; formaldehyde-aniline; butyraldehyde-aniline; and heptaldehyde-aniline.

Suitable substituted ureas include trimethylthiourea; diethylthiourea; dibutylthiourea; tripentylthiourea; 1,3-bis(2-benzothiazolylmercaptomethyl)urea; and N,N-diphenylthiourea.

Suitable substituted guanidines include diphenylguanidine; di-o-tolylguanidine; diphenylguanidine phthalate; and the di-o-tolylguanidine salt of dicatechol borate.

Suitable substituted xanthates include zinc ethylxanthate; sodium isopropylxanthate; butylxanthic disulfide; potassium isopropylxanthate; and zinc butylxanthate.

Suitable dithiocarbamates include copper dimethyl-, zinc dimethyl-, tellurium diethyl-, cadmium dicyclobexyl-, lead dimethyl-, lead dimethyl-, selenium dibutyl-, zinc pentamethylene-, zinc didecyl-, and zinc isopropyloctyl-dithiocarbamate.

Suitable thiazoles include 2-mercaptobenzothiazole, zinc mercaptothiazolyl mercaptide, 2-benzothiazolyl-N,N-diethylthiocarbamyl sulfide, and 2,2'-dithiobis(benzothiazole).

Suitable imidazoles include 2-mercaptoimidazoline and 2-mercapto-4,4,6-trimethyldihydropyrimidine.

Suitable sulfenamides include N-t-butyl-2-benzothiazole-, N-cyclohexylbenzothiazole-, N,N-diisopropylbenzothiazole-, N-(2,6-dimethylmorpholino)-2-benzothiazole-, and N,N-diethylbenzothiazole-sulfenamide.

Suitable thiuramidisulfides include N,N'-diethyl-, tetrabutyl-, N,N'-diisopropyldioctyl-, tetramethyl-, N,N'-dicyclobexyl-, and N,N'-tetralauryl-thiuramidisulfide.

In the case of substantially random/pseudorandom interpolymers not including the optional diene component, peroxide cure systems are preferred; in the case of substantially random/pseudorandom interpolymers including the optional diene component, sulfur-based (for example, containing sulfur, a dithiocarbamate, a thiazole, an imidazole, a sulfenamide, a thiuramidisulfide or combinations thereof) and phenolic cure systems are preferred.

Preparation of Thermoplastic Vulcanizates

The thermoset compositions of the invention may be incorporated into polyolefins to form thermoplastic vulcanizates. The proportions of ingredients utilized will vary somewhat with the particular polyolefin employed, with the desired application, as well as with the character of the crosslinked substantially random/pseudorandom interpolymers and compounding ingredients. Typically, as the amount of the crosslinked substantially random/pseudorandom interpolymers increases, the stiffness of the resultant thermoplastic vulcanizate decreases. The thermoplastic vulcanizates of the invention will typically comprise from 10 to 90 weight percent of the polyolefin and from 10 to 90 weight percent of the crosslinked substantially random/pseudorandom interpolymers.

Suitable polyolefins include thermoplastic, crystalline, high molecular weight polymers prepared by the polymerization of one or more monoolefins. Examples of suitable polyolefins include ethylene and the isotactic and syndiotactic monoolefin polymer resins, such as propylene, 1-butene, 1-pentene, 1-hexene, 2-methyl-1-propene, 3-methyl-1-pentene, 4-methyl-1-pentene, 5-methyl-1-hexene and mixtures thereof. Most typically, the thermoplastic vulcanizates of the invention will utilize isotactic polypropylene as the polyolefin component.

The thermoplastic vulcanizates of the invention are preferably prepared by dynamic vulcanization, wherein a mixture of the noncrosslinked substantially random/pseudorandom interpolymer is mixed with the polyolefin resin and an appropriate curing agent to form a blend, which is then masticated at vulcanization temperature. In particular, the noncrosslinked substantially random/pseudorandom interpolymer is blended with a polyolefin at a temperature above the melting point of the polyolefin. After the substantially random/pseudorandom interpolymer and polyolefin are intimately mixed, an appropriate curing agent is added, such as are described above with respect to the compounding and curing of the substantially random/pseudorandom interpolymers. The blend is subsequently masticated using conventional masticating equipment, such as a Banbury mixer, Brabender mixer, or a mixing extruder. The temperature of the blend during mastication is that sufficient to effect vulcanization of the substantially random/pseudorandom interpolymer. A suitable range of vulcanization temperatures is from the melting temperature of the polyolefin resin (120°C in the case of polyethylene and 175°C in the case of polypropylene) to the temperature at which the substantially random/pseudorandom interpolymer, the polyolefin, or the curing agent degrades. Typical temperatures are from 180°C to 250°C, preferably from 180°C to 200°C.

Methods other than the dynamic vulcanization of the substantially random/pseudorandom interpolymer/polyolefin are likewise suitable. For instance, the substantially random/pseudorandom interpolymer may be crosslinked prior to introduction to the polyolefin. The crosslinked substantially random/pseudorandom interpolymer may then be powdered and mixed with the polyolefin at a temperature above the melting or softening point of the polyolefin. Provided that the crosslinked substantially random/pseudorandom interpolymer particles are small, well-dispersed, and in an appropriate concentration, (that is, provided an intimate mixture of the crosslinked substantially random/pseudorandom interpolymer and polyolefin is achieved), the thermoplastic vulcanizates of the invention may be readily obtained. Should such an intimate mixture not be achieved, the resultant product will contain visually observable islands of the crosslinked substantially random/pseudorandom interpolymer. In this case, the part may be comminuted by pulverizing or by cold milling to reduce particle size to below 50 microns. Upon adequate comminution, the particles may be remolded into a part exhibiting more uniform composition and the enhanced properties characteristic of the thermoplastic vulcanizates of the invention.

The thermoplastic vulcanizates of the invention may include various additives, such as carbon black, silica, titanium dioxide, colored pigments, clay, zinc oxide, stearic acid, accelerators, vulcanizing agents, sulfur, stabilizers, antidegradants, processing aids, adhesives, tackifiers, plasticizers, wax, prevulcanization inhibitors, discontinuous fibers (such as wood cellulose fibers) and extender oils. Such additives may be provided either prior to, during, or subsequent to vulcanization.

As in the case of the thermoset elastomers of the invention, carbon black will preferably be added to the blend of the substantially random/pseudorandom interpolpolymer and polyolefin prior to vulcanization. Carbon black will typically be provided in an amount from 0 to 50 weight percent, typically from 0.5 to 50 weight percent, based on the total formulation weight. When the carbon black is employed to mask a color, it is typically employed in the range of 0.5 to 10 weight percent, based on the total weight of the formulation. When the carbon black is employed to increase toughness and/or decrease cost, it is typically employed in amounts greater than 10 weight percent, based on the total weight of the formulation.

Moreover, as in the case of the thermoset elastomers of the invention, one or more extender oils will preferably be added to the blend of the substantially random/pseudorandom interpolpolymer and polyolefin prior to vulcanization. Suitable extender oils are listed in Rubber World Blue Book 1975 Edition, Materials and Compounding Ingredients for Rubber, pages 145-190. Typical classes of extender oils include aromatic, naphthenic, and paraffinic extender oils. The extender oil(s) will typically be provided in an amount from 0 to 50 weight percent based on the total formulation weight. When employed, the extender oil will typically be provided in an amount of at least 5 weight percent, more typically in an amount of from 15 to 25 weight percent, based on the total weight of the formulation.

In one preferred embodiment, the thermoplastic vulcanizates of the invention will comprise from 30 to 60 weight percent of the substantially random/pseudorandom interpolpolymer, from 15 to 55 weight percent of the thermoplastic polyolefin, and from 15 to 30 weight percent of the extender oil. Such thermoplastic vulcanizates are particularly useful as moldings for automotive applications.

In a particularly preferred embodiment, the thermoplastic vulcanizates of the invention are characterized by an ASTM #2 oil swell of less than 60 percent, as determined by ASTM D-471.

Test Procedures

Monomer contents are determined by carbon-13 NMR spectroscopy.

Stress-strain properties are determined on an Instron model 1122 load frame using 0.870 inch (2.2 cm) micro-tensile samples measured at an extension rate of 5 inch/min (12.7 cm/min). Tensile break, elongation at break, and 100 percent modulus are measured in accordance with ASTM D-412.

Melt index is measured in accordance with ASTM D-1238.

Molecular weight and molecular weight distribution are determined by gel permeation chromatography.

ASTM #2 and #3 oil swells are measured in accordance with ASTM D-471.

Hardness shore "A" is measured in accordance with ASTM D-2240.

Compression set is measured in accordance with ASTM D-395.

Example One: Preparation of Ethylene-Styrene Interpolymers and Thermoset Elastomers

5 Ethylene/styrene copolymers were made using (tert-butylamido)dimethyl(tetramethyl- η 5-cyclopenta-dienyl)silane dimethyltitanium(+4) catalyst and tris(pentafluorophenyl)borane cocatalyst in a one to one ratio according to the following procedure. A two liter reactor was charged with 360 grams (500 mL) of ISOPAR™ E mixed alkane solvent (available from Exxon Chemicals Inc.) and the desired amount of styrene comonomer. Hydrogen was added to the reactor by differential pressure expansion
10 from a 75 mL addition tank. The reactor was heated to the run temperature and was saturated with ethylene at the desired pressure. (Tert-butylamido)dimethyl-(tetramethyl- η 5-cyclopentadienyl)silane dimethyltitanium (IV) catalyst and tris(pentafluorophenyl)borane cocatalyst were mixed in a dry box by pipeting the desired amount of a 0.005 M solution of the tris(pentafluorophenyl)borane cocatalyst in ISOPAR™ E mixed alkane solvent or toluene into a solution of the (tert-butylamido)dimethyl-
15 (tetramethyl- η 5-cyclopentadienyl)silane dimethyl-titanium (IV) catalyst in ISOPAR™ E mixed alkane solvent or toluene. The resulting catalyst solution was transferred to a catalyst addition tank and was injected into the reactor.

The polymerization was allowed to proceed, with ethylene being introduced on demand. Additional charges of catalyst and cocatalyst, if used, were prepared in the same manner and were added
20 to the reactor periodically. The total amount of catalyst employed was set forth in Table One. In each instance, the amount of tris(pentafluorophenyl)borane cocatalyst (on a molar basis) equals the amount of (tert-butylamido)dimethyl-(tetramethyl- η 5-cyclopentadienyl)silane dimethyltitanium (IV) catalyst indicated in Table One. After the run time, the polymer solution was removed from the reactor and quenched with isopropyl alcohol. A hindered phenol antioxidant (IRGANOX™ 1010 (available from
25 Ciba Geigy Corp.) was added to the polymer. Volatiles were removed from the polymer in a reduced pressure vacuum oven at 135°C for 20 hours.

The preparation conditions for the substantially random interpolymers were set forth in Table 1.

Sample	Catalyst amount μ (-mol)	ISOPAR™ -E (mL)	Styrene (mL)	Ethylene (psig)	Hydrogen (Δ psi)	Reaction Temp (°C)	Reaction Time (min)	Yield (g)
ES-1	2.5	250	750	300	0	80	10	32.3
ES-2	3.8	500	500	200	0	80	10	28.8
ES-3	15.0	500	500	200	100	60	30	166

The resultant substantially random interpolymers were characterized as being pseudorandom and linear.

30 The interpolymers were compounded and cured according to the following procedure. The 60 gram bowl of a Brabender PS-2 internal mixer was preheated to 120°F. 100 pph carbon black N550 (available from Cabot Corporation), 50 pph SUNPAR™ 2280 oil (available from Sun Oil), 5 pph

paraffin wax, 1 pph stearic acid, 8 pph Vul-Cup 40KE peroxide (available from Hercules) and 1.5 pph triallyl cyanurate coagent (available from American Cyanamid) were premixed in a plastic or paper container. The resultant blend was loaded into the 60 gram bowl. To the bowl was further added 100 pph of the desired substantially random/pseudorandom interpolymers as prepared above. The ram was lowered on the internal mixer, and the compound was allowed to mix until a temperature of 220°F was reached (approximately five minutes). The compound was removed from the mixer and was optionally roll-milled.

The samples were compression molded at 260°F to obtain uncured (green) test plaques. The uncured (green) test plaques were compression mold cured at 340°F for 20 minutes to obtain crosslinked thermoset elastomer compositions.

The stress-strain properties of the neat interpolymers, of the uncured (green) test plaques, and of the crosslinked thermoset elastomer compositions were set forth in Table Two. Therein, the designation "ND" means that the given property was not determined.

	ES-1	ES-2	ES-3	C1 (Tafmer 680-P)	C2 (V-457)	C3 (V-707)
COMONOMER CONTENT (AS DIRECTED BY NMR)						
wt % ethylene	67.5	56.8	48.0		51.0	70.0
wt % styrene	32.5	43.2	52.0		0	0
wt % propylene	0	0	0		49.0	30.0
STRESS-STRAIN PROPERTIES OF NEAT UNCROSSLINKED POLYMERS						
tensile at break (psi)	3200	2156	1390	668	243	887
100% modulus (psi)	759	445	256	170	75	205
elongation at break (%)	395	420	518	1115	1780	1336
melt index at 190°C (g/10 min)	0.8	0.8	10.2	4.0	7.1	3.9
Mw/Mn	2.07	2.14	3.50	21.8	3.07	4.59
GREEN STRESS-STRAIN PROPERTIES						
tensile at break (psi)	ND	ND	594	460	70	459
100% modulus (psi)	ND	ND	315	264	52	231
elongation at break (%)	ND	ND	453	476	84	685
STRESS-STRAIN PROPERTIES OF CROSSLINKED INTERPOLYMERS						
tensile at break (psi)	3156	ND	1005	1994	1236	1569
100% modulus (psi)	1076	ND	532	506	276	674
elongation at break (%)	300	ND	297	383	409	292

As illustrated in Table Two, the crosslinked thermoset elastomer compositions of the invention exhibit a higher 100 % modulus than the comparative materials C1 (Tafmer™ 680-P (available from

Mitsui Petrochemical)) and C2 (Vistalon™ 457 (available from Exxon Chemical Co.)). This was consistent with the significantly higher 100 % modulus exhibited by the neat interpolymers as compared to the comparative materials.

Example Two: Preparation of Ethylene/Styrene/Ethylidene Norbornene Interpolymers and Thermoset Elastomers

Ethylene/styrene/ethylidene norbornene interpolymers were made using (tert-butylamido)dimethyl-(tetramethyl- η 5-cyclopenta-dienyl)silane dimethyltitanium(+4) catalyst and tris(pentafluorophenyl)borane cocatalyst in a one to one ratio according to the following procedure. A two liter reactor was charged with 360 grams (500 mL) of ISOPAR™ E mixed alkane solvent (available from Exxon Chemicals Inc.) and the desired amount of styrene comonomer. Ethylidene norbornene was transferred to the reactor. Hydrogen was added to the reactor by differential pressure expansion from a 75 mL addition tank. The reactor was heated to the run temperature and was saturated with ethylene at the desired pressure. (Tert-butylamido)dimethyl-(tetramethyl- η 5-cyclopentadienyl)silane dimethyltitanium (IV) catalyst and tris(pentafluoro-phenyl)borane cocatalyst were mixed in a dry box by pipeting the desired amount of a 0.005 M solution of the tris(pentafluorophenyl)borane cocatalyst in ISOPAR™ E mixed alkane solvent or toluene into a solution of the (tert-butylamido)dimethyl-(tetramethyl- η 5-cyclopentadienyl)silane dimethyl-titanium (IV) catalyst in ISOPAR™ E mixed alkane solvent or toluene. The resulting catalyst solution was transferred to a catalyst addition tank and was injected into the reactor.

The polymerization was allowed to proceed, with ethylene being introduced on demand. Additional charges of catalyst and cocatalyst, if used, were prepared in the same manner and were added to the reactor periodically. The total amount of catalyst employed was reported in Table Three. In each instance, the amount of tris(pentafluoro-phenyl)borane cocatalyst (on a molar basis) was equal to that of the (tert-butylamido)dimethyl-(tetramethyl- η 5-cyclopentadienyl)silane dimethyltitanium (IV) catalyst as indicated in Table Three. After the run time, the polymer solution was removed from the reactor and quenched with isopropyl alcohol. A hindered phenol antioxidant (IRGANOX™ 1010 (available from Ciba Geigy Corp.) was added to the polymer. Volatiles were removed from the polymer in a reduced pressure vacuum oven at 135°C for 20 hours.

The preparation conditions for the ethylene/styrene/ethylidene norbornene interpolymers were set forth in Table Three.

Sample	Catalyst amount (-mol)	ISOPAR -E (mL)	Styrene (mL)	ENB amount (mL)	Ethylene pressure (psig)	Hydrogen (psi)	Reaction Temp (C)	Reaction Time (min)	Yield (g)
ES-1	15	500	500	50	250	100	65	20	149.9
ES-2	12.5	500	500	75	300	100	65	30	120.7
ES-3	10	500	500	25	200	100	65	30	135.1

The resultant substantially random interpolymers were characterized as being pseudorandom and linear.

The interpolymers were compounded and cured according to the following procedure. The 60 gram bowl of a Brabender PS-2 internal mixer was preheated to 120°F. 100 pph carbon black N550 (available from Cabot), 50 pph SUNPARTM 2280 oil (available from Sun Oil), 5 pph paraffin wax, 1 pph stearic acid, 5 pph zinc oxide, 1.5 pph sulfur, and 0.5 pph Captax 2-mercaptobenzothiazole (available from R. T. Vanderbilt) were premixed in a plastic or paper container. The resultant blend was loaded into the 60 gram bowl. To the bowl was further added 100 pph of the desired interpolymers as prepared above. The ram was lowered on the internal mixer, and the compound was allowed to mix until a temperature of 220°F was reached (approximately five minutes). The compound was removed from the mixer and was optionally roll-milled.

The samples were compression molded at 260°F to obtain uncured (green) test plaques. The uncured (green) test plaques were compression mold cured at 340°F for 20 minutes to obtain crosslinked thermoset elastomer compositions.

As between ESDM1(a)-(d), ESDM1(a) was prepared in accordance with the above formulation. ESDM1(b)-(d) were likewise prepared in accordance with the above formulation, except that in the case of ESDM1(b), 50 pph SUNDEX 750T oil (available from Sun Oil), was used in place of the SUNPAR oil; in the case of ESDM1(c), 50 pph trioctyltrimellitate was used in place of the SUNPAR oil; and in the case of ESDM1(d), 0.75 pph (rather than 1.5 pph) sulfur was employed.

Regarding the comparative materials, C4 was prepared using the formulation provided above, with Vistalon 6505 EPDM (available from Exxon) being used in place of the substantially random/pseudorandom interpolymers. C5 was prepared using the formulation provided above, with EPSyn 70A EPDM (available from DSM Copolymer) being used in place of the substantially random/pseudorandom interpolymers used in the present invention. C6(a) was prepared using the formulation provided above, with SBR 1500 styrene butadiene rubber being used in place of the substantially random/pseudorandom interpolymers and Sundex 750T oil (available from Sun Oil) being used in place of the SUNPAR oil. C6(b) was prepared using the formulation provided above, except that SBR 1500 styrene butadiene rubber was used in place of the substantially random/pseudorandom interpolymers, 50 pph (rather than 100 pph) N550 carbon black was employed, 7 pph Sundex 750T oil (rather than 50 pph SUNPAR 2280 oil) was employed.

The stress-strain properties of the neat interpolymers, of the uncured (green) test plaques, and of the crosslinked thermoset elastomer compositions were set forth in Table Four. Therein, the abbreviation "ND" means that a given property was not determined.

	ESDM-1	ESDM-2	ESDM-3	C4	C5	C6
COMONOMER CONTENT AS DETERMINED BY (C- NMR)						
wt % ethylene	50.9	46.7	49.4	50	50	0
wt % styrene	35.3	43.7	44	0	0	24
wt % diene	13.8	9.6	6.6	12	10	0
wt % propylene		0	0	38	40	0
wt % butadiene		0	0	0	0	76
STRESS-STRAIN PROPERTIES OF NEAT UNCROSSLINKED INTERPOLYMERS						
tensile at break (psi)	1884	1345	1021	83	80	31
100% modulus (psi)	319	212	242	81	75	30
elongation at break (%)	513	566	505	288	300	>400
melt index (g/10min)	1.6	8.0	4.6	<2.0	<0.5	ND
GREEN STRESS- STRAIN PROPERTIES	a b c d	ND	ND	ND	ND	a b
tensile at break (psi)	869 723 859 932	ND	ND	78	80	3 61
100% modulus (psi)	570 457 606 469	ND	ND	32	67	14 51
elongation at break (%)	338 395 276 369	ND	ND	250	130	2129 300
STRESS-STRAIN AND OIL RESISTANCE PROPERTIES COMPOUNDED CROSS-LINKED INTERPOLYMERS	a b c d					a b
tensile at break (%)	2379 2279 2451 2033	ND	ND	2044	2399	1575 1475
100% modulus	1455 1395 1539 1018	ND	ND	598	533	295 386
elongation at break (%)	188 219 183 246	ND	ND	318	401	277 392
ASTM #2 oil swell (70 hours @ 212°F)	54 55 54 62	ND	ND	93	100	57 49
STRESS STRAIN PROPERTIES AFTER AN OVEN AGING FOR 70 HOURS AT 250°F	a b c d					a b
tensile at break (psi)	2697 2907 ND 2507	ND	ND	ND	ND	663 1352
100% modulus (psi)	2143 ND ND 1401	ND	ND	ND	ND	ND 1326
elongation at break (%)	34 84 ND 199.6	ND	ND	ND	ND	93 103
PERCENT CHANGE IN STRESS-STRAIN PROPERTIES AFTER OVEN AGING 70 HOURS AT 250°F	a b c d					a b
tensile at break (%)	+15 +28 ND +24	ND	ND	ND	ND	-58 -8
100% modulus (%)	-47 ND ND +38	ND	ND	ND	ND	ND +378
elongation at break (%)	-29 -62 ND -19	ND	ND	ND	ND	-76 -74

As illustrated in Table Four, the crosslinked thermoset elastomers of the invention typically exhibit a highly improved 100% modulus, as compared to comparative materials C4 (Vistalon™ 6505 EPDM (available from Exxon)), C5 (EPSyn 70A EPDM (available from DSM Copolymer)) and C6 (SBR 1500 styrene-butadiene rubber).

5 As further illustrated in Table Four, the crosslinked thermoset elastomers of the invention typically exhibit a resistance to oil swell similar to that of styrene-butadiene-rubber, but superior to that of EPDM materials.

As further illustrated in Table Four, the crosslinked thermoset elastomers of the invention exhibit aging properties superior to those of styrene-butadiene rubber. For instance, upon aging at 250°F 10 for 70 hours in an air oven, the crosslinked ethylene/styrene/ethylidene norbornene interpolymers exhibited increased tensile at break values and moderately decreased elongation at break values. In contrast, upon oven aging under the same conditions, the styrene-butadiene rubbers exhibited decreased tensile at break values and significantly decreased elongation at break values.

Thus, as illustrated in Table Four, the crosslinked ethylene/styrene/diene thermoset elastomers 15 of the invention exhibit a resistance to oil swell characteristic of styrene-butadiene rubber without suffering the concomitant negative effects of heat aging.

Example Three: Preparation of Thermoplastic Vulcanizates

The Brabender PS-2 or Haake internal torque mixer was preheated to 350°C. The desired amount of Pro-fax 6524 isotactic polypropylene (available from Himont Incorporated) was added to the 20 mixer, and was allowed to melt and to homogenize. Over one minute, the desired amount of the noncrosslinked substantially random/pseudorandom interpolymers was added. Thereafter, the process oil, antioxidant, stearic acid, and carbon black were added and mixed for one minute. The zinc oxide, sulfur, benzothiazyl disulfide and methyl tuads were added. Mixing occurs until the torque reaches a maximum and for at least 10 minutes total mix time. The resultant thermoplastic vulcanizate was 25 removed from the mixer.

In executing the above procedure, the formulations set forth in Table Five were employed. Unless otherwise indicated, all amounts were expressed in parts per hundred, based on 100 parts of the elastomer.

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Elastomer	TPV-1	TPV-2				C-TPV-1	C-TPV-2
	ESDM-2	ESDM-3				C-4	C-5
wt % ethylene	46.7	49.4				50	50
wt % styrene	43.7	44				0	0
wt % diene	9.6	6.6				12	10
wt % propylene	0	0				38	40
TPV formulation (all amounts in pph)		A	B	C	D		
Substantially random interpolymers	100	100	100	100	100	100	100
isotactic polypropylene	67	67	33	67	100	67	67
process oil	50	50	100	100	100	50	50
IRGANOX 1010 antioxidant (available from Ciba Geigy Corp.)	3	3	3	3	3	3	3
stearic acid	1	1	1	1	1	1	1
N550 carbon black available from Cabot	1	1	1	1	1	1	1
zinc oxide	5	5	5	5	5	5	5
sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5
benzothiazyl disulfide (available from Altax)	0.38	0.38	0.38	0.38	0.38	0.38	0.38
methyl tads	0.75	0.75	0.75	0.75	0.75	0.75	0.75

Except in the case of TPV1(b), SunPar™ 2280 (available from Sun Oil) was employed as the process oil. For TPV1(b), trioctyltrimellitate was employed as the process oil.

- 5 The resultant thermoplastic vulcanizates were compression molded at 380°F. Representative physical properties of the thermoplastic vulcanizates and of comparative thermoplastic vulcanizates C-TPV1 (made with Vistalon 6505 EPDM (available from Exxon)) and C-TPV2 (made with EPSyn 70A EPDM (available from DSM Rubber)) were set forth in Table Six. Therein, the abbreviation "ND" means that a given property was not determined.

	TPV 1		TPV 2				C-TPV-1	C-TPV-2
Stress-Strain properties	A	B	A	B	C	D		
tensile at break (psi)	1507	1589	1621	515	1549	1436	1520	1787
100% modulus (psi)	1375	1307	951	327	691	1008	759	889
elongation at break (%)	132	164	251	192	336	247	322	344
ASTM #2-70 hours at 212°F (% swell)	ND	ND	109.5	133.8	89.3	68.2	ND	ND
Hardness Shore "A"	88	86	86	63	77	83	90	88

- 10 A comparison of TPV1(a) and TPV2(a) with comparative materials C-TPV1 (made with Vistalon 6505 EPDM (available from Exxon)) and C-TPV2 (made with EPSyn 70A EPDM (available from DSM Rubber)) indicates that the thermoplastic vulcanizates of the invention exhibit a much greater resistance to oil swell (under the ASTM #2 test method) than the comparative materials without sacrificing hardness (Hardness Shore "A"). A comparison of these materials further indicates that the

thermoplastic vulcanizates of the invention exhibit improved 100% modulus values and comparable tensile at break values, with respect to the comparative materials.

5 A comparison of TPV-2(b), TPV-2(c), and TPV-2(d) indicates that one can adjust resistance to ASTM #2 oil swell and hardness values by adjusting the ratio between the polypropylene and the substantially random/pseudorandom interpolymer. Namely, as the proportion of the polypropylene increases, the resistance to ASTM #2 oil swell and hardness likewise increase. Moreover, the effect of the added substantially random/pseudorandom interpolymer was evident. In particular, the percent elongation at break of the inventive thermoplastic vulcanizates was many times greater than that of unmodified isotactic polypropylene, which exhibits a percent elongation at break of 13 percent.

10 The thermoset elastomers of the invention were useful in a variety of applications. Exemplary applications include hoses, air ducts, brake cups, roofing materials, as well as use as components in blends as impact modifiers and in general molded goods.

The thermoplastic vulcanizates were likewise useful in a variety of applications, particularly articles made by extrusion, injection molding and compression molding techniques. One principal application for the TPVS of the invention was in automotive under-the-hood components, such as rack-and-pinion boots and ducting, fuel-line covers, hoses, belts, and gaskets. Other expected automotive applications were in interior applications (such as skins, instrument panels, air-bag covers, door trim, control knobs, molded parts, and seat belt covers) and exterior applications (such as tires and molding).

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CLAIMS

1. A thermoset elastomer comprising either

(1) a crosslinked pseudorandom interpolymers of:

- (a) from 15 to 70 weight percent of at least one α -olefin,
- 5 (b) from 30 to 70 weight percent of at least one vinylidene aromatic compound, and
- (c) from 0 to 15 weight percent of at least one diene; or (2) a crosslinked substantially

random interpolymers of:

- (a) from 15 to 70 weight percent of at least one α -olefin,
- (b) from 30 to 70 weight percent of at least one vinylidene aromatic compound, and
- 10 (c) from 0 to 15 weight percent of at least one diene.

2. The thermoset elastomer of Claim 1 comprising either

(1) a crosslinked pseudorandom interpolymers of

- (a) from 25 to 60 weight percent of at least one α -olefin,
- 15 (b) from 35 to 60 weight percent of at least one vinylidene aromatic compound, and
- (c) from 3 to 15 weight percent of at least one diene, or

(2) a crosslinked substantially random interpolymers of

- (a) from 25 to 60 weight percent of at least one α -olefin,
- (b) from 35 to 60 weight percent of at least one vinylidene aromatic compound, and
- 20 (c) from 3 to 15 weight percent of at least one diene, or

(2) a crosslinked substantially random interpolymers of.

3. The thermoset elastomer of Claim 1 comprising either (1) a crosslinked pseudorandom interpolymers of:

- 25 (a) from 40 to 65 weight percent of at least one α -olefin selected from the group consisting of ethylene, propylene, 1-butene, 3-methyl-1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 5-methyl-1-hexene, 4-ethyl-1-hexene, 1-octene, 1-dodecene, 3-phenylpropene, and mixtures thereof; and

- (b) from 35 to 60 weight percent of at least one vinylidene aromatic compound selected from
30 the group consisting of styrene, α -methylstyrene, ortho-methylstyrene, meta-methylstyrene, para-methylstyrene, chlorostyrene, vinylbenzocyclobutane, and divinylbenzene, and mixtures thereof; or

(2) a crosslinked substantially random interpolymers of:

- 35 (a) from 40 to 65 weight percent of at least one α -olefin selected from the group consisting of ethylene, propylene, 1-butene, 3-methyl-1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene,

5-methyl-1-hexene, 4-ethyl-1-hexene, 1-octene, 1-dodecene, 3-phenylpropene, and mixtures thereof; and

- (b) from 35 to 60 weight percent of at least one vinylidene aromatic compound selected from the group consisting of styrene, α -methylstyrene, ortho-methylstyrene, meta-methylstyrene, para-methylstyrene, chlorostyrene, vinylbenzocyclobutane, and divinylbenzene, and mixtures thereof.

4. The thermoset elastomer of Claim 1, 2, or 3 wherein

- (a) the α -olefin is selected from the group consisting of ethylene, propylene, 1-butene, 3-methyl-1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 5-methyl-1-hexene, 4-ethyl-1-hexene, 1-octene, 1-dodecene, 3-phenylpropene, and mixtures thereof;
- (b) the vinylidene aromatic compound is selected from the group consisting of styrene, α -methylstyrene, ortho-methylstyrene, meta-methylstyrene, para-methylstyrene, chlorostyrene, vinylbenzocyclobutane, and divinylbenzene, and mixtures thereof; and
- (c) the diene, when present, is selected from the group consisting of butadiene, 1,3-pentadiene, 1,4-pentadiene, isoprene, 1,4-hexadiene, 7-methyl-1,6-octadiene, dicyclopentadiene, methylenenorbornene, ethylenenorbornene, and methyltetrahydroindene, and mixtures thereof.

5. The thermoset elastomer of Claim 4, wherein the α -olefin is ethylene, the

vinylidene aromatic compound is styrene, and the diene, when present, is ethylenenorbornene.

6. A process for preparing a thermoset elastomer comprising:

- (a) reacting at least one α -olefin with at least one vinylidene aromatic compound and optionally at least one diene, in the presence of a constrained geometry catalyst, to form a pseudorandom interpolpolymer;
- (b) curing the pseudorandom interpolpolymer to form a thermoset elastomer.

7. The process of Claim 6, wherein the constrained geometry catalyst comprises a metal coordination complex comprising a metal of Group III or IV or the Lanthanide series of the Periodic Table of the Elements and a delocalized Π -bonded moiety substituted with a constrain-inducing moiety, said complex having a constrained geometry the metal atom such that the angle at the metal between the centroid of the delocalized, substituted Π -bonded moiety and the center of at least one remaining substituent is less than such angle in a similar complex containing a similar Π -bonded moiety lacking in such constrain-inducing substituent, and provided further that for such complexes comprising more than one delocalized, substituted π -bonded moiety, only one thereof for each metal atom of the complex is a cyclic, delocalized, substituted Π -bonded moiety.

8. The process of Claim 6, wherein the constrained geometry catalyst is selected from the group consisting of (tert-butylamido)(tetramethyl- η 5-cyclopentadienyl)-1,2-ethanediylzirconium dichloride; (tert-butylamido) (tetramethyl- η 5-cyclopentadienyl)-1,2-ethanediyltitanium dichloride; (tert-butylamido)dimethyl(tetramethyl- η 5-cyclopentadienyl) silanetitanium dimethyl; (tert-butylamido)dimethyl(tetramethyl- η 5-indenyl) silanetitanium dimethyl; (tert-butylamido)dimethyl(tetramethyl- η 5-tetrahydroindenyl) silanetitanium dimethyl; (tert-butylamido)dimethyl(tetramethyl- η 5-fluorenyl) silanetitanium dimethyl; (tert-butylamido)dimethyl(tetramethyl- η 5-tetrahydrofluorenyl) silanetitanium dimethyl; (tert-butylamido)dimethyl(tetramethyl- η 5-octahydrofluorenyl) silanetitanium dimethyl; (tert-butylamido)dimethyl(tetramethyl- η 5-cyclopentadienyl) silanetitanium dibenzyl; (tert-butylamido)dimethyl (tetramethyl- η 5-cyclopentadienyl)silanezirconium dibenzyl; and mixtures thereof.

9. The process of Claim 7, wherein the constrained geometry catalyst is activated by a cocatalyst selected from the group consisting of polymeric alumoxanes, oligomeric alumoxanes, polymeric carbylboranes, oligomeric carbylboranes, monomeric carbylboranes, aluminum alkyls, aluminum halides, haloaluminum alkyls, substituted ammonium salts, silver salts, ferrocenium ions, and mixtures thereof.

10. The process of Claim 7, wherein the constrained geometry catalyst is activated by tris(pentafluorophenyl)borane.

11. The process Claim 6, wherein the curing is effected by a curing agent selected from the group consisting of peroxides, phenols, azides, aldehyde-amine reaction products, substituted ureas, substituted guanidines, substituted xanthates, substituted dithiocarbamates, thiazoles, imidazoles, sulfenamides, thiuramidisulfides, paraquinonedioxime, dibenzoparaquinonedioxime, and sulfur.

12. The process of Claim 6, wherein the curing is effected by a curing agent selected from the group consisting of peroxides, phenols, substituted dithiocarbamates, thiazoles, imidazoles, sulfenamides, thiuramidisulfides, sulfur and mixtures thereof and sulfur.

13. The process of Claim 6, wherein the curing is effected simultaneously with the compounding of the pseudorandom interpolymers.

14. A process for preparing a thermoset elastomer comprising:

- (a) reacting at least one α -olefin with at least one vinylidene aromatic compound and optionally at least one diene, in the presence of a constrained geometry catalyst, to form a substantially random interpolpolymer;
- (b) curing the substantially random interpolpolymer to form a thermoset elastomer.

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15. The process of Claim 6, 7, 8, 9, 10, 11, 12, 13 or 14, wherein

- (i) the α -olefin is selected from the group consisting of ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 5-methyl-1-hexene, 4-ethyl-1-hexene, 1-octene, 3-phenylpropene, and mixtures thereof;
- 10 (ii) the vinylidene aromatic compound is selected from the groups consisting of styrene, α -methylstyrene, ortho-methylstyrene, meta-methylstyrene, para-methylstyrene, chlorostyrene, vinylbenzocyclobutane, divinylbenzene, and mixtures thereof; and
- (iii) the diene, when present, is selected from the group consisting of butadiene, 1,3-pentadiene, 1,4-pentadiene, isoprene, 1,4-hexadiene, 7-methyl-1,6-octadiene, dicyclopentadiene,
- 15 methylenenorbornene, ethylenenorbornene, and mixtures thereof.

16. A thermoplastic vulcanizate comprising:

- (a) a crosslinked pseudorandom interpolpolymer of
 - (i) from 15 to 70 weight percent of at least one α -olefin,
 - 20 (ii) from 30 to 70 weight percent of at least one vinylidene aromatic compound, and
 - (iii) from 0 to 15 weight percent of at least one diene; and
- (b) at least one thermoplastic polyolefin.

17. The thermoplastic vulcanizate of Claim 16, comprising from 10 to 90 weight percent of the crosslinked pseudorandom interpolpolymer and from 10 to 90 weight percent of the thermoplastic polyolefin.

18. The thermoplastic vulcanizate of Claim 16, further comprising from 0 to 50 weight percent of an extender oil selected from the group consisting of aromatic oils, naphthenic oils, and paraffinic oils.

19. The thermoplastic vulcanizate of Claim 16, wherein the crosslinked pseudorandom interpolpolymer is an interpolpolymer of (a) from 40 to 65 weight percent of at least one α -olefin, and (b) from 35 to 60 weight percent of at least one vinylidene aromatic compound.

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20. The thermoplastic vulcanizate of Claim 18, wherein the crosslinked pseudorandom interpolmer is an interpolmer of (a) from 25 to 60 weight percent of at least one α -olefin, (b) from 35 to 60 weight percent of at least one vinylidene aromatic compound, and (c) from 3 to 15 weight percent of at least one diene.

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21. The thermoplastic vulcanizate of Claim 16, comprising from 30 to 60 weight percent of the crosslinked pseudorandom interpolmer, from 15 to 55 weight percent of the thermoplastic polyolefin, and from 15 to 30 weight percent of the extender oil.

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22. A thermoplastic vulcanizate comprising:

(a) a crosslinked substantially random interpolmer of

(i) from 15 to 70 weight percent of at least one α -olefin,

(ii) from 30 to 70 weight percent of at least one vinylidene aromatic compound, and

(iii) from 0 to 15 weight percent of at least one diene; and

15

(b) at least one thermoplastic polyolefin.

23. The thermoplastic vulcanizate of Claim 16, 17, 18, 19, 20, 21 or 22, wherein:

(a) the α -olefin is selected from the group consisting of ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 5-methyl-1-hexene, 4-ethyl-1-hexene, 1-octene, 3-phenylpropene, and mixtures thereof;

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(b) the vinylidene aromatic compound is selected from the group consisting of styrene, α -methylstyrene, ortho-methylstyrene, meta-methylstyrene, para-methylstyrene, chlorostyrene, vinylbenzocyclobutane, divinylbenzene, and mixtures thereof; and

(c) the optional diene is selected from the group consisting of butadiene, 1,3-pentadiene, 1,4-pentadiene, isoprene, 1,4-hexadiene, 7-methyl-1,6-octadiene, dicyclopentadiene, methylenenorbornene, ethylenenorbornene, methyltetrahydroindene, and mixtures thereof.

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24. The thermoplastic vulcanizate of Claim 23, wherein the thermoplastic polyolefin is selected from the group consisting of ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 2-methyl-1-propene, 3-methyl-1-pentene, 4-methyl-1-pentene, 5-methyl-1-hexene, and mixtures thereof.

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25. The thermoplastic vulcanizate of Claim 23, wherein the α -olefin is ethylene, the vinylidene aromatic compound is styrene, and the diene, when present, is ethylenenorbornene.

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26. The thermoplastic vulcanizate of Claim 24, wherein the α -olefin is ethylene, the vinylidene aromatic compound is styrene, and the diene, when present, is ethylenenorbornene.

27. A thermoplastic vulcanizate comprising a crosslinked substantially random
interpolymer of at least one α -olefin, at least one vinylidene aromatic compound and optionally at least
one diene distributed in a thermoplastic polyolefin matrix, said thermoplastic vulcanizate being
5 characterized by an ASTM #2 oil swell of less than 60 percent, as determined by ASTM D-471.

28. A process for making a thermoplastic vulcanizate comprising:

(a) reacting at least one α -olefin with at least one vinylidene aromatic compound and optionally at
least one diene in the presence of a constrained geometry catalyst to form a pseudorandom
10 interpolymer;

(b) intimately mixing the pseudorandom interpolymer with at least one thermoplastic polyolefin at a
temperature above the melting or softening point of the thermoplastic polyolefin;

(c) providing to the intimate mixture an agent for curing the pseudorandom interpolymer;

(d) simultaneously curing the pseudorandom interpolymer and compounding the intimate mixture to
15 form a thermoplastic vulcanizate.

29. The process of Claim 28, wherein

(i) the α -olefin is selected from the group consisting of ethylene, propylene, 1-butene, 1-pentene, 1-
hexene, 4-methyl-1-pentene, 5-methyl-1-hexene, 4-ethyl-1-hexene, 1-octene, 3-phenylpropene,
20 and mixtures thereof;

(ii) the vinylidene aromatic compound is selected from the group consisting of styrene, α -
methylstyrene, ortho-methylstyrene, meta-methylstyrene, para-methylstyrene, chlorostyrene,
vinylbenzocyclobutane, divinylbenzene, and mixtures thereof; and

(iii) the optional diene is selected from the group consisting of butadiene, 1,3-pentadiene, 1,4
25 pentadiene, isoprene, 1,4-hexadiene, 7-methyl-1,6-octadiene, dicyclopentadiene,
methylenenorbornene, ethylenenorbornene, methyltetrahydroindene, and mixtures thereof.

30. The process of Claim 28, wherein the thermoplastic polyolefin is selected
from the group consisting of ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 2-methyl-1-propene, 3-
30 methyl-1-pentene, 4-methyl-1-pentene, 5-methyl-1-hexene, and mixtures thereof.

31. The process of Claim 28, wherein the agent for curing the substantially
random interpolymer is selected from the group consisting of peroxides, phenols, azides, aldehyde-
amine reaction products, substituted ureas, substituted guanidines, substituted xanthates, substituted
35 dithiocarbamates, thiazoles, imidazoles, sulfenamides, thiuramdisulfides, paraquinonedioxime,
dibenzoparaquinonedioxime, sulfur, and mixtures thereof.

32. The process of Claim 28, 29, 30 or 31, wherein the constrained geometry catalyst comprises a metal coordination complex comprising a metal of Group III or IV or the Lanthanide series of the Periodic Table of the Elements and a delocalized Π -bonded moiety substituted with a constrain-inducing moiety, said complex having a constrained geometry the metal atom such that the angle at the metal between the centroid of the delocalized, substituted Π -bonded moiety and the center of at least one remaining substituent is less than such angle in a similar complex containing a similar Π -bonded moiety lacking in such constrain-inducing substituent, and provided further that for such complexes comprising more than one delocalized, substituted π -bonded moiety, only one thereof for each metal atom of the complex is a cyclic, delocalized, substituted Π -bonded moiety.

33. The process of Claim 32, wherein the constrained geometry catalyst is activated by a cocatalyst selected from the group consisting of polymeric alumoxanes, oligomeric alumoxanes, polymeric carbylboranes, oligomeric carbylboranes, monomeric carbylboranes, aluminum alkyls, aluminum halides, haloaluminum alkyls, ammonium salts, silver salts, ferrocenium ions, and mixtures thereof.

34. A process for making a thermoplastic vulcanizate comprising:

- (a) reacting at least one α -olefin with at least one vinylidene aromatic compound and optionally at least one diene in the presence of a constrained geometry catalyst to form a substantially random interpolpolymer;
- (b) intimately mixing the substantially random interpolpolymer with at least one thermoplastic polyolefin at a temperature above the melting or softening point of the thermoplastic polyolefin;
- (c) providing to the intimate mixture an agent for curing the substantially random interpolpolymer;
- (d) simultaneously curing the substantially random interpolpolymer and compounding the intimate mixture to form a thermoplastic vulcanizate.

35. A fabricated part comprising a crosslinked pseudorandom interpolpolymer of:

- (a) from 15 to 70 weight percent of at least one α -olefin selected from the group consisting of ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 5-methyl-1-hexene, 4-ethyl-1-hexene, 1-octene, 3-phenylpropene, and mixtures thereof;
- (b) from 30 to 70 weight percent of at least one vinylidene aromatic compound selected from the groups consisting of styrene, α -methylstyrene, ortho-methylstyrene, meta-methylstyrene, para-methylstyrene, chlorostyrene, vinylbenzocyclobutane, divinylbenzene, and mixtures thereof;
- (c) from 0 to 15 weight percent of at least one diene selected from the group consisting of butadiene, 1,3-pentadiene, 1,4-pentadiene, isoprene, 1,4-hexadiene, 7-methyl-1,6-octadiene,

dicyclopentadiene, methylenenorbornene, ethylenenorbornene, methyltetrahydroindene, and mixtures thereof.

36. A fabricated part comprising a thermoplastic vulcanizate comprising
- 5 (a) from 10 to 90 weight percent of a crosslinked substantially random interpolymer of
- (i) from 15 to 70 weight percent of at least one α -olefin selected from the group consisting of ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 5-methyl-1-hexene, 4-ethyl-1-hexene, 1-octene, 3-phenylpropene, and mixtures thereof;
- 10 (ii) from 30 to 70 weight percent of at least one vinylidene aromatic compound selected from the groups consisting of styrene, α -methylstyrene, ortho-methylstyrene, meta-methylstyrene, para-methylstyrene, chlorostyrene, vinylbenzocyclobutane, divinylbenzene, and mixtures thereof; and
- 15 (iii) from 0 to 15 weight percent of at least one diene selected from the group consisting of butadiene, 1,3-pentadiene, 1,4-pentadiene, isoprene, 1,4-hexadiene, 7-methyl-1,6-octadiene, dicyclopentadiene, methylenenorbornene, ethylenenorbornene, methyltetrahydroindene, and mixtures thereof; and
- (b) from 10 to 90 weight percent of at least one thermoplastic polyolefin selected from the group consisting of ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 2-methyl-1-propene, 3-methyl-1-pentene, 4-methyl-1-pentene, 5-methyl-1-hexene, and mixtures thereof.

Elastomers suitable for use over a broad range of temperatures and which are also less susceptible to ozone degradation are desired. Thermoset elastomers which are prepared from elastomers having high green strength (which provides greater flexibility in their handling prior to curing) are particularly desired. Also desired, are thermoset elastomers which are resistant to oil, which are useful in fabricated parts which typically contact oil, such as automotive parts and gaskets. Also desired are thermoset elastomers which easily undergo surface modification, to promote surface adhesion of the elastomer and/or to provide ionic sites on the elastomer surface. Also desired is a process for preparing such thermoset elastomers.

Thermoplastic vulcanizates are crystalline polyolefinic matrices through which thermoset elastomers are generally uniformly distributed. Examples of thermoplastic vulcanizates include EPM and EPDM thermoset materials distributed in a crystalline polypropylene matrix. Such thermoplastic vulcanizates are disadvantageous, in that they are susceptible to oil degradation. Thermoplastic vulcanizates which are more resistant to oil are desired. Also desired is a process for preparing such thermoplastic vulcanizates.

Summary of Invention

The subject invention provides a thermoset elastomer comprising a crosslinked substantially random interpolmer of: (a) from 15 to 70 weight percent of at least one α -olefin, (b) from 30 to 70 weight percent of at least one vinylidene aromatic compound, and (c) from 0 to 15 weight percent of at least one diene.

The subject invention further provides a process for making a thermoset elastomer comprising: (a) reacting at least one α -olefin with at least one vinylidene aromatic compound in the presence of a constrained geometry catalyst to form a substantially random interpolmer; and (b) curing the substantially random interpolmer to form a thermoset elastomer.

The subject invention further provides a thermoplastic vulcanizate comprising a blend of: (1) a crosslinked substantially random interpolmer of (a) from 15 to 70 weight percent of at least one α -olefin, (b) from 30 to 70 weight percent of at least one vinylidene aromatic compound, and (c) from 0 to 15 weight percent of at least one diene; and (2) at least one thermoplastic polyolefin.

The subject invention further provides a process for making a thermoplastic vulcanizate comprising:

- (a) reacting at least one α -olefin with at least one vinylidene aromatic compound and optionally at least one diene in the presence of a constrained geometry catalyst to form a substantially random interpolmer;
- (b) intimately mixing the substantially random interpolmer with at least one thermoplastic polyolefin at a temperature above the melting or softening point of the thermoplastic polyolefin;
- (c) providing to the intimate mixture an agent for curing the substantially random interpolmer;

(d) simultaneously curing the substantially random interpolymer and compounding the intimate mixture to form a thermoplastic vulcanizate.

The subject invention further comprises fabricated parts comprising the thermoset elastomers or thermoplastic vulcanizates of the invention.

5 These and other embodiments are more fully described in the following Detailed Description.

The term "polymer" as used herein refers to a polymeric compound prepared by polymerizing monomers whether of the same or a different type. The generic term polymer thus embraces the term homopolymer, usually employed to refer to polymers prepared from only one type of monomer, and the term interpolymer as defined hereinafter.

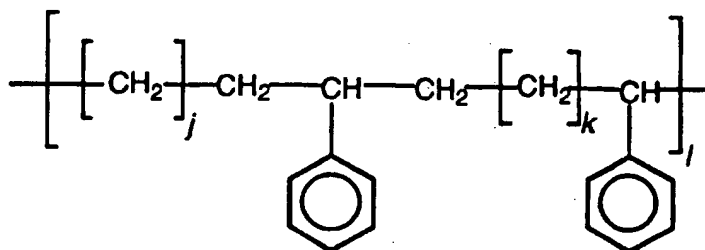
10 The term "interpolymer" as used herein refers to polymers prepared by the polymerization of at least two different types of monomers. The generic term interpolymer thus includes copolymers, usually employed to refer to polymers prepared from two different monomers, and polymers prepared from more than two different types of monomers.

15 Statements herein that a polymer or interpolymer comprises or contains certain monomers, mean that such polymer or interpolymer comprises or contains polymerized therein units derived from such a monomer. For example, if a polymer is said to contain ethylene monomer, the polymer will have incorporated in it an ethylene derivative, that is, $-\text{CH}_2-\text{CH}_2-$.

20 The elastomeric thermoset compositions of the invention are preferably substantially random substantially linear or linear interpolymers comprising an olefin and a vinylidene aromatic monomer, which interpolymers have been crosslinked to yield thermoset behavior. As used herein, the term "substantially random" means that the distribution of the monomers of the interpolymer can be described by the Bernoullian statistical model or by a first or second order Markovian statistical model, as described by J. C. Randall in Polymer Sequence Determination, Carbon-13 NMR Method, Academic Press New York, 1977, pp. 71-78. Substantially random interpolymers do not contain more than 15 weight percent of the total amount of vinylidene aromatic monomer in blocks of more than three vinylidene aromatic monomer units.

25 Pseudorandom interpolymers are a subset of substantially random interpolymers. Pseudorandom interpolymers are characterized by an architecture in which all phenyl (or substituted phenyl) groups which are pendant from the polymer backbone are separated by two or more carbon backbone units. In other words, the pseudorandom interpolymers of the invention, in their noncrosslinked state, can be described by the following general formula (using styrene as the vinylidene aromatic monomer and ethylene as the α -olefin for illustration):

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Noncrosslinked pseudorandom interpolymers are described in European Patent Publication 416,815-A, the relevant parts of which are incorporated herein by reference.

While not wishing to be bound by any particular theory, it is believed that during the addition polymerization reaction of, for example, ethylene and styrene, in the presence of a constrained geometry catalyst as described below, if a styrene monomer is inserted into the growing polymer chain, the next monomer inserted will be an ethylene monomer or a styrene monomer inserted in an inverted or "tail-to-tail" fashion. It is believed that after an inverted or "tail-to-tail" styrene monomer is inserted, the next monomer will be ethylene, as the insertion of a second styrene monomer at this point would place it too close to the inverted styrene monomer, that is, less than two carbon backbone units away.

Preferably, the substantially random/pseudorandom interpolymers will be characterized as largely atactic, as indicated by a ^{13}C -NMR spectrum in which the peak areas corresponding to the main chain methylene and methine carbons representing either meso diad sequences or racemic diad sequences does not exceed 75 percent of the total peak area of the main chain methylene and methine carbons.

The substantially random/pseudorandom interpolymers may further be characterized as either linear or substantially linear. As used herein, the term "substantially linear" means that the interpolymers is characterized as having long chain branches. In contrast, the term "linear" means that the interpolymers lacks long chain branches.

Substantially linear interpolymers are characterized as having a melt flow ratio, I_{10}/I_2 (as determined by ASTM D-1238) ≥ 5.63 , a molecular weight distribution (as determined by gel permeation chromatography) $M_w/M_n \leq (I_{10}/I_2) - 4.63$, and either a critical shear rate at the onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear olefin polymer having about the same I_2 and M_w/M_n or a critical shear rate at the onset of gross melt fracture of greater than about 4×10^6 dynes/cm 2 .

To identify the melt fracture phenomena, an apparent shear stress vs. apparent shear rate plot may be employed. According to Ramamurthy in Journal of Rheology, 30(2),337-357, 1986, above a certain critical flow rate, the observed extrudate irregularities may be broadly classified into two main types: surface melt fracture and gross melt fracture.

Surface melt fracture occurs under apparently steady flow conditions and ranges in detail from loss of specular gloss to the more severe form of "sharkskin". As used herein, the onset of surface melt

INTERNATIONAL SEARCH REPORT

International application No.

PC1/US 95/09945

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08F 212/00, C08F 210/00, C08L 23/02, C08L 25/02 // C08F 4/602, 4/74
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, PAJ, WPI, CLAIMS, CAPLUS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP, A1, 0634427 (MITSUI PETROCHEMICAL INDUSTRIES, LTD.), 18 January 1995 (18.01.95), page 3, line 33 - line 37; page 19, line 4 - line 55, claims 1-5, 9	1-36
Y	--	16-34, 36
X	WO, A1, 9406858 (THE DOW CHEMICAL COMPANY), 31 March 1994 (31.03.94), page 5, line 30 - page 6, line 2; page 6, line 19 - line 26; page 11, line 13 - line 27; page 12, line 20; claim 11; abstract	1-15, 35
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:	* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* "A" document defining the general state of the art which is not considered to be of particular relevance	* "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* "B" earlier document but published on or after the international filing date	* "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* "&" document member of the same patent family
* "O" document referring to an oral disclosure, use, exhibition or other means	
* "P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

Date of mailing of the international search report

21 November 1995

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 95/09945

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Dialog Information Services, file 351, DERWENT WPI, Dialog accession no. 009584777, WPI accession no. 93-278323/35, IDEMITSU KOSAN CO LTD: "Olefinic copolymer for elastomers, high tenacity material and complex materials - prepd. by copolymerising styre- nic monomer and olefin in catalyst contg. transition metal and organo metallic cpds., for modified copo- lymers mfr.", & JP, A, 5194666, 930803, 9335 (Basic) abstract --	1-15
X	EP, A2, 0572990 (MITSUI TOATSU CHEMICALS, INC.), 8 December 1993 (08.12.93), page 5, line 3 - line 10, abstract --	1-10, 14-15
Y	US, A, 4130535 (AUBERT Y. CORAN ET AL), 19 December 1978 (19.12.78), column 2, line 1 - line 19; column 2, line 64 - column 3, line 15; column 5, line 48 - line 66; column 6, line 10 - line 16 and line 41 - line 46; abstract --	16-34, 36
A	EP, A2, 0416815 (THE DOW CHEMICAL COMPANY), 13 March 1991 (13.03.91), claim 33, abstract -----	1-36

INTERNATIONAL SEARCH REPORT

Information on patent family members

SA 15721

International application No.

02/10/95

PCT/US 95/09945

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A1- 0634427	18/01/95	NONE	
WO-A1- 9406858	31/03/94	NONE	
EP-A2- 0572990	08/12/93	NONE	
US-A- 4130535	19/12/78	AT-B- 361704	25/03/81
		AU-B, B- 506201	20/12/79
		BE-A, A- 844318	20/01/77
		CA-A- 1101578	19/05/81
		CH-A- 643279	30/05/84
		DE-A, C, C 2632654	10/02/77
		FR-A, B- 2323734	08/04/77
		GB-A- 1524602	13/09/78
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